

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Salts of Polyvalent Metals and Alkylsalicylic Acids

5 We, SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ N.V., a company organised
under the laws of The Netherlands, of 30
Carel van Bylandtlaan, The Hague, The
Netherlands, do hereby declare the invention,
for which we pray that a patent may be
granted to us, and the method by which it is
to be performed, to be particularly described
in and by the following statement:—

10 The invention relates to salts of polyvalent
metals and alkylsalicylic acids as novel com-
pounds and to processes to prepare these com-
pounds. The invention also relates to the
application of these compounds as additives
in, for example, lubricants and fuels.

15 The co-pending British patent application
No. 29775/67 (Serial No. 1,146,925) relates
to lubricant compositions with improved dis-
persant properties at high temperatures, com-
prising one or more lubricants and one or more
20 salts of polyvalent metals and alkylsalicylic
acids, which alkylsalicylic acids contain at
least one alkyl group with more than 12
carbon atoms and of which more than 60%
25 consists of acids with an alkyl group that is
attached to the benzene nucleus in para posi-
tion relative to the hydroxyl group.

As possible modes of preparation for these
salts the specification pertaining to the said
30 application describes four routes starting from
phenol, ortho- and para-cresol and salicylic
acid, which are elucidated in the examples.
Of these routes the one starting from phenol
is economically the most attractive. According
35 to the example relating to this mode of pre-
paration, phenol is alkylated with cetane and
the alkylphenols thus obtained are converted
into the corresponding alkylsalicylic acids by
phenation, carboxylation and hydrolysis. This
40 process yields a mixture of alkylsalicylic acids
of which 88%_m contains an alkyl group that
is attached to the benzene nucleus in para

position relative to the hydroxyl group. These
acids can be converted in a simple manner into
the desired salts.

For the preparation of the salts on a
technical scale the use pure cetane as alkyla-
tion agent is obviously less attractive from
an economic point of view. For this purpose
technical products such as technical olefin
50 mixtures would seem to be better suited. Ac-
cording to the examples given in the afore-
mentioned specification, which relate to the
preparation of the salts starting from salicylic
acid and ortho- and para-cresol, satisfactory
55 results can be obtained with technical C₁₂—
C₁₈ olefin mixtures as alkylation agent.

Continued investigation has now shown that
if these technical olefin mixtures are used for
the alkylation of phenol, the alkylate thus
60 obtained, contains besides the desired alkyla-
tion products 4-alkylphenol and 2,4-dialkyl-
phenol a considerable quantity of 2-alkyl-
phenol. If this alkylate is converted in the
usual manner into a mixture of salts of poly-
65 valent metals and alkylsalicylic acids, this
mixture contains a high proportion of salts of
3-alkylsalicylic acid originating from the 2-
alkylphenol. As described in the aforemen-
tioned specification, the latter salts, after in-
70 corporation in a lubricant, do not show a
significant improvement in dispersant prop-
erties at high temperatures over mixtures of
salts of polyvalent metals and alkylsalicylic
acids known already at the moment of filing
75 of said application.

Efforts to find a suitable way to decrease
the quantity of 2-alkylphenol in the alkylate
have so far failed. For example, it was tried
to increase the quantity of 2,4-dialkylphenol
80 at the cost of the quantity of 2-alkylphenol,
formed during alkylation by applying more
severe alkylation conditions (higher alkylation
temperature and larger excess of olefins).

However, this only led to an increase in percentage of non-carboxylatable 2,4,6-trialkylphenol in the alkylate, whilst the yield of 2,4-dialkylphenol hardly increased. Another possibility investigated was the separation of the 2-alkylphenol from the mixture of alkylphenols. The separation, which calls for a high-vacuum distillation and is relatively expensive, leads, when carried out on a technical scale, only to separation between mono- and dialkylphenols, so that in this way not only the undesired 2-alkylphenol, but also the 4-alkylphenol which is very suitable for further conversion into alkylsalicylic acid is removed from the alkylphenol mixture.

It has now been found that in the preparation of salts of polyvalent metals and alkylsalicylic acids by alkylation of phenol followed by phenation, carboxylation, hydrolysis and salt formation, the formation of a substantial amount of salt of 3-alkylsalicylic acid can be prevented if the alkylation is completely or partly carried out with an alkylation agent which attaches preferentially to the benzene nucleus in para position relative to the hydroxyl group. These alkylation agents have such a structure that the alkyl group attaching to the benzene nucleus through their application, is attached to it with a quaternary carbon atom.

The salts obtained as described above are novel compounds.

The invention therefore relates to salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group with more than 12 carbon atoms and of which more than 60% consists of acids containing an alkyl group that is attached to the benzene nucleus in para position relative to the hydroxyl group, while at least part of the latter alkyl groups is attached with a quaternary carbon atom to the benzene nucleus.

Alkylation agents having such a structure that the alkyl group which attaches to the benzene nucleus as a result of their application, is attached to it with a quaternary carbon atom, will for the sake of brevity be indicated hereinafter as "tertiary alkylation agents".

In the preparation of the salts by alkylation of phenol, conversion of the alkylphenols into the alkylsalicylic acids and forming the salts of these alkylsalicylic acids, the alkylation can be carried out in various ways. For example, phenol may be alkylated with a tertiary alkylation agent containing more than 12 carbon atoms in the molecule. As examples of such tertiary alkylation agents may be mentioned monoolefins which are branched at one or both of the carbon atoms adjacent to the double bond, such as tetraisobutene and higher polyisobutenes or precursors for these olefins such as monohydroxyalkanes in which the hydroxyl group is attached to a tertiary carbon

atom or occurs in an α -position relative to a tertiary carbon atom in the molecule.

The alkylation of phenol is preferably carried out in two stages using a different alkylation agent in each stage, one of which is a tertiary alkylation agent with at most 12 carbon atoms in the molecule and the other an alkylation agent containing a hydrocarbon group with more than 12 carbon atoms. Examples of suitable tertiary alkylation agents are in this case monoolefins with at most 12 carbon atoms in the molecule which are branched at one or both of the carbon atoms adjacent to the double bond or precursors for these olefins. Very suitable are monoolefins with the general formula



in which R represents an alkyl group with at most 9 carbon atoms, such as isobutene, isopentene and isohexene, in particular isobutene. Examples of suitable alkylation agents which can be used in combination with the above-mentioned tertiary alkylation agents are straight-chain olefins with more than 12 carbon atoms in the molecule. Very suitable are technical mixtures of straight-chain monoolefins with more than 12 carbon atoms in the molecule, in particular technical olefin mixtures with more than 12 carbon atoms in the molecule obtained in cracking straight-chain paraffins obtained by means of urea extraction.

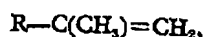
Alkyl groups attached with a quaternary carbon atom to the benzene nucleus, such as tertiary butyl groups, show the tendency to shift under the prevailing alkylation conditions (for example a shift from the para to the ortho position). This shift plays a greater part according as the alkylate is longer in contact with the alkylation catalyst. As the two-stage alkylation of phenol has as its primary purpose to obtain a maximum yield of para-substituted material, the contact between the para-tert-alkylphenol and the alkylation catalyst should be as short as possible. In this connection the two-stage alkylation of phenol as hereinbefore described is preferably carried out in such a way that the tertiary alkylation agent is applied in the second stage.

Acid-activated clays have been found to be very suitable catalysts for the alkylation of phenol and the alkylphenols. The quantity of catalyst used is as a rule 1—10%w, in particular 3—7%w relative to the sum of the quantities by weight of alkylation agent and phenol to be alkylated.

The alkylation of phenol with straight-chain monoolefins having more than 12 carbon atoms in the molecule is preferably carried out at temperatures between 175 and 225°C. One preferably uses 0.6 to 1.0 mole of olefin per mole of phenol.

The alkylation of the alkylphenols with

branched monoolefins having the general formula



5 in which R represents an alkyl group with at most 9 carbon atoms, is preferably carried out at temperatures between 50 and 200°C. One uses preferably 1.0 to 1.5 mole of olefin per mole of alkylphenol.

10 The conversion of the alkylphenols thus prepared into the corresponding alkylsalicylic acids can be effected according to the techniques known in the art for this conversion. An attractive process is, for example, the following.

15 Using an alcoholic caustic solution the alkylphenols are converted into the corresponding alkylphenates, which are treated with CO₂ at about 140°C and a pressure of 10 to 30 atm. The alkylsalicylic acids can be liberated from the alkyl salicylates thus obtained by means of, for example, 30% sulphuric acid.

20 The salts according to the invention can be very suitably used as additives, for example in lubricants and fuels. They are of special importance as additives in lubricating oils, because they are capable of keeping the interior of engine cylinders, in particular diesel engine cylinders, clean, and of counteracting deposition of carbonaceous products on pistons and in piston ring grooves.

30 When the salts according to the invention are used as lubricating oil additives one preferably chooses basic salts, because these salts, in addition to their dispersant action, are capable of neutralizing acid compounds formed during the combustion process in the engine. A basicity of the polyvalent metal salts up to 250% is for this purpose in most cases sufficient. Favourable results can, for example, be obtained by using polyvalent metal salts of the present type with a basicity between 25 and 225%, e.g. polyvalent metal salts with a basicity of about 50% or of about 200%.

45 Among the salts of polyvalent metals and alkylsalicylic acids suitable as additives for lubricating oils, the salts of bivalent metals are particularly eligible. Preference is given to salts of alkaline earth metals and in particular to calcium salts.

50 The conversion of the alkylsalicylic acids into neutral as well as basic salts can be effected according to techniques generally applied for these conversions. For the preparation of neutral calcium salts the alkylsalicylic acids can, for example, be converted into the corresponding sodium salts, which are then allowed to react with an equivalent quantity of CaCl₂. For the preparation of basic calcium salts with a relatively low basicity, for example 50%, one can treat the alkylsalicylic acids with 2 equivalents of calcium in the form of Ca(OH)₂. For the preparation of basic calcium salts with a higher basicity, for ex-

ample 200%, the alkylsalicylic acids can be 65 treated with 4 equivalents of calcium in the form of Ca(OH)₂, while introducing 1.6 equivalents of CO₂.

As stated hereinbefore, the metal salts 70 should have been derived from alkylsalicylic acids containing at least one alkyl group more than 12 carbon atoms. For application in lubricating oils one chooses preferably metal salts of alkylsalicylic acids containing at least one alkyl group with at least 14 carbon atoms, such as metal salts of alkylsalicylic acids containing an alkyl group with 15—18 carbon atoms. 75

With respect to the molar percentage of the acids containing an alkyl group attached to the benzene nucleus in para position relative to the hydroxyl group, it may be further observed that special interest is in salts of alkylsalicylic acids in which the molar percentage is more than 70% m. 80

85 The lubricating oils in which the present salts can be incorporated as additives may be mineral lubricating oils of varying viscosity, but also synthetic lubricating oils or lubricating oils containing fatty oils. The salts may also be added to lubricating greases. The salts are of particular importance to improve the quality of mineral lubricating oils or mixtures thereof. The salts of polyvalent metals and alkylsalicylic acids can be incorporated as such in the lubricating oils or in the form of a concentrate that has been obtained, for example, by mixing the salts with a small quantity of oil. The concentration of the present metal salts in the lubricating oils may vary within wide limits. In general, the desired dispersancy is obtained if the lubricating oils contain 0.01 to 5% w, in particular 0.1 to 1% w of polyvalent metal in the form of the present salts of polyvalent metals and alkylsalicylic acids. 100 In addition to salts of polyvalent metals and alkylsalicylic acids, the lubricating oil compositions may contain other additives, such as antioxidants, foam inhibitors, anti-corrosion agents, viscosity and/or viscosity index improvers, agents to improve the lubricating action and other substances which are usually added to lubricating oils. 105

The invention will now be elucidated by means of the following examples. 110

Example A and B are reference examples.

Example I and II are examples according to the present invention. The C₁₂—C₁₈ olefin mixture used in Example B, I and II was a technical mixture of straight-chain monoolefins with 15 to 18 carbon atoms, in the molecule, obtained in cracking straight-chain paraffins obtained by means of urea extraction. 120

EXAMPLE A

(according to UK patent application No. 29775/67—Serial No. 1,146,925). 125

Phenol was alkylated at 150°C with cetane (molar ratio 1:2.5 using 5% w of acid clay

as catalyst. The alkylphenols thus obtained were converted into the corresponding alkylsalicylic acids by phenation, carboxylation and

hydrolysis. In this way 1 mole of phenol yielded 0.65 mole of alkylsalicylic acids with the following composition:

12% m of 3-cetylsalicylic acid
12% m of 5-cetylsalicylic acid
76% m of 3,5-dicetylsalicylic acid } 88% m para-substituted

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EXAMPLE B

Phenol was alkylated at 200°C with a mixture of C_{12} — C_{18} olefins (molar ratio 1:2.5) using 5% w of acid clay as catalyst. The alkylphenols thus obtained were converted into the

corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. In this way 1 mole of phenol yielded 0.50 mole of alkylsalicylic acids with the following composition:

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36% m of 3-(C_{12} — C_{18}) alkylsalicylic acid
16% m of 5-(C_{12} — C_{18}) alkylsalicylic acid
48% m of 3,5-di(C_{12} — C_{18}) alkylsalicylic acid } 64% m para-substituted

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EXAMPLE I

Phenol was alkylated at 200°C with a mixture of C_{12} — C_{18} olefins (molar ratio 1.3:1) using 5% w of acid clay as catalyst. The alkylphenols thus obtained were subsequently alkylated with isobutene (molar ratio 1:1.1), again with 5% w of acid clay as catalyst. The alkyl-

phenols obtained in this second alkylation were converted into the corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. In this way 1 mole of C_{12} — C_{18} olefins yielded 0.50 mole of alkylsalicylic acids with the following composition:

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5% m of 3-(C_{12} — C_{18}) alkylsalicylic acid
24% m of 5-(C_{12} — C_{18}) alkylsalicylic acid
9% m of 3,5-di(C_{12} — C_{18}) dialkylsalicylic acid
38% m of 3-(C_{12} — C_{18}) alkyl-5-tert. butylsalicylic acid
24% m of 3-tert. butyl-5-(C_{12} — C_{18}) alkylsalicylic acid } 95% m para-substituted

The alkylsalicylic acids obtained were converted into calcium salts with a basicity of 50 and 200% w.

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EXAMPLE II

Phenol was alkylated at 200°C with a mixture of C_{12} — C_{18} olefins (molar ratio 1.3:1) with 5% w of acid clays as catalyst. The alkylphenols thus obtained were subsequently alkylated at 130°C with isobutene (molar ratio 1:1.1), again with 5% w of acid clay as

catalyst. The alkylphenols obtained in this second alkylation were converted into the corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. In this way 1 mole of C_{12} — C_{18} olefins yielded 0.5 mole of alkylsalicylic acids with the following composition:

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12% m of 3-(C_{12} — C_{18}) alkylsalicylic acid
18% m of 5-(C_{12} — C_{18}) alkylsalicylic acid
9% m of 3,5-di(C_{12} — C_{18}) alkylsalicylic acid
33% m of 3-(C_{12} — C_{18}) alkyl-5-tert. butylsalicylic acid
28% m of 3-tert. butyl-5-(C_{12} — C_{18}) alkylsalicylic acid } 88% m para-substituted

The alkylsalicylic acid obtained were converted into calcium salts with a basicity of 50 and 200% w.

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WHAT WE CLAIM IS:—

1. Salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group with more than 12 carbon atoms and of which more than 60% m consists of acids containing an alkyl group in

para position relative to the hydroxyl group, while at least part of the latter alkyl groups is attached with a quaternary carbon atom to the benzene nucleus.

2. Salts as claimed in claim 1, which are basic salts.

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3. Salts as claimed in claim 2, which have a basicity below 250%.
4. Salts as claimed in claim 3, which have a basicity between 25 and 225%.
- 5 5. Salts as claimed in any one of claims 1—4, which are salts of bivalent metals.
6. Salts as claimed in claim 5, which are alkaline earth metal salts.
7. Salts as claimed in claim 6, which are calcium salts.
- 10 8. Salts as claimed in any one of claims 1—7, which are salts of alkylsalicylic acids containing at least one alkyl group with 15—18 carbon atoms.
- 15 9. Salts as claimed in any one of claims 1—8, which are salts of alkylsalicylic acids consisting at least partly of acids containing a tert.-butyl group in para position relative to the hydroxyl group.
- 20 10. Salts as claimed in any one of claims 1—9, which are salts of alkylsalicylic acids of which more than 70% consists of acids containing an alkyl group in para position relative to the hydroxyl group.
- 25 11. Salts substantially as described hereinbefore and in particular with reference to Examples I and II.
12. A process for the preparation of salts of polyvalent metals and alkylsalicylic acids as claimed in any one of claims 1—11, by alkylation of phenol, conversion of the alkylphenols into the alkyl salicylic acids and forming the salts of these alkylsalicylic acids, the alkylation of phenol being completely or in part carried out with a tertiary alkylation agent as hereinbefore defined.
- 30 13. A process as claimed in claim 12, in which the alkylation is carried out in two stages using a different alkylation agent, in each stage one of which is a tertiary alkylation agent with at most 12 carbon atoms in the molecule and the other an alkylation agent with more than 12 carbon atoms in the molecule.
- 40 14. A process as claimed in claim 13, in which the tertiary alkylation agent is a monoolefin or a mixture of monoolefins with at most 12 carbon atoms in the molecule, which monoolefins are branched at one or both of the carbon atoms adjacent to double bond or precursors for these olefins.
- 45 15. A process as claimed in claim 14, in which the tertiary alkylation agent is a monoolefin or a mixture of monoolefins with the general formula
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$$R-C(CH_3)=CH_2,$$
- in which R represents an alkyl group with at most 9 carbon atoms.
- 60 16. A process as claimed in claim 15, in which the tertiary alkylation agent is isobutene.
17. A process as claimed in any one of claims 13—16, in which the alkylation agent with more than 12 carbon atoms in the molecule, is a straight-chain monoolefin or a mixture of straight-chain monoolefins.
- 65 18. A process as claimed in claim 17, in which the alkylation agent with more than 12 carbon atoms in the molecule, is a technical mixture of straight-chain monoolefins.
- 70 19. A process as claimed in claim 18, in which the alkylation agent with more than 12 carbon atoms in the molecule is a technical olefin mixture obtained in cracking straight-chain paraffins obtained by means of urea extraction.
- 75 20. A process as claimed in claims 13—19, in which the tertiary alkylation agent is used in the second alkylation stage.
21. A process as claimed in claim 20, in which phenol is alkylated in the first stage with one or more straight-chain monoolefins with more than 12 carbon atoms in the molecule in a molar ratio of 0.6 to 1.0 mole of olefin per mole of phenol and the alkylphenols thus obtained are subsequently alkylated in the second stage with one or more branched monoolefins with the general formula
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$$R-C(CH_3)=CH_2,$$
- in which R represents an alkyl group with at most 9 carbon atoms, in a molar ratio of 1.0 to 1.5 mole of olefin per mole of alkylphenol.
- 85 22. A process as claimed in claim 21, in which the alkylation in the first stage is carried out at a temperature of between 175 and 225°C and the alkylation in the second stage at a temperature of between 50 and 200°C.
23. A process as claimed in any one of claims 12—22, in which the alkylation is carried out in the presence of an acid-activated clay as catalyst.
- 90 24. A process as claimed in claim 23, in which the quantity of acid-activated clay is 1—10%w, in particular 3—7%w, relative to the sum of the quantities by weight of alkylation agent and phenol to be alkylated.
- 105 25. A process for the preparation of salts of polyvalent metals and alkylsalicylic acids, substantially as described hereinbefore and with special reference to Examples I and II.
- 110 26. Lubricant compositions containing one or more lubricants and one or more salts of polyvalent metals and alkylsalicylic acids as claimed in any one of claims 1—11.
- 115 27. Lubricant compositions as claimed in claim 26, in which the lubricant is a mineral lubricating oil or a mixture of mineral lubricating oils.
- 120 28. Lubricant compositions as claimed in claims 26 and 27, containing 0.01 to 5%w and in particular 0.1 to 1%w of polyvalent metal in the form of a salt of polyvalent metal and an alkylsalicylic acid.
- 125 29. A process for the preparation of lubricant compositions as claimed in any one of claims 26—28 by incorporation of one or more

salts of polyvalent metals and alkylsalicylic
acids in a lubricant or mixture of lubricants.

30. A process for lubricating diesel engines
using a lubricant composition as claimed in

5 claims 26—28.

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